Binuclear metallapyrrolidone complexes formed from coupling of CO and alkynes with the .mu.3-nitrene ligand of Ru3(.mu.3-NPh)(CO)10

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position (*endo*-2-*d*), undergo exchange with THF in the time required for the carbonylation of 1 to proceed to completion. In addition no deuterium kinetic isotope effect is observed when 1-*d* is carbonylated in THF to give *endo*-2.

From the results presented here, it is concluded that the reaction between 1 and CO proceeds by a mechanism different from the intramolecular mechanism proposed for the reaction of (η^6-C_6H_6)Mn$(CO)_2CH_3$ and $P(C_6H_5)_3$.[5] In THF the reaction apparently does not involve direct intermolecular transfer of hydride from 1 because carbonylation of 1-*d* leads to the formation of no *endo*-2-*d*. This conclusion is consistent with the absence of a deuterium kinetic isotope effect. Since neither 1-*d* nor *endo*-2-*d* exchanges with THF during the reaction period, the formation of product, by hydride ion or hydrogen atom transfer from 1 to the exo position in the product, would be expected to display deuterium tracing and a deuterum kinetic isotope effect when 1-*d* is used. The observations in THF suggest that an undetected intermediate or intermediates, probably of very low concentration, are involved in product formation. A detailed FTIR study, designed to identify intermediates and to establish the mechanism of this reaction, is in progress.

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Registry No. 1, 91230-53-4; *endo*-2, 65700-52-9.

Supplementary Material Available: Stereoviews, tables of crystal data, anisotropic thermal parameters, and fractional coordinates and isotropic thermal parameters, and complete listings of bond lengths and bond angles (6 pages); a listing of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

Binuclear Metallapyrrolidone Complexes Formed from Coupling of CO and Alkynes with the μ_3-Nitrene Ligand of $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$

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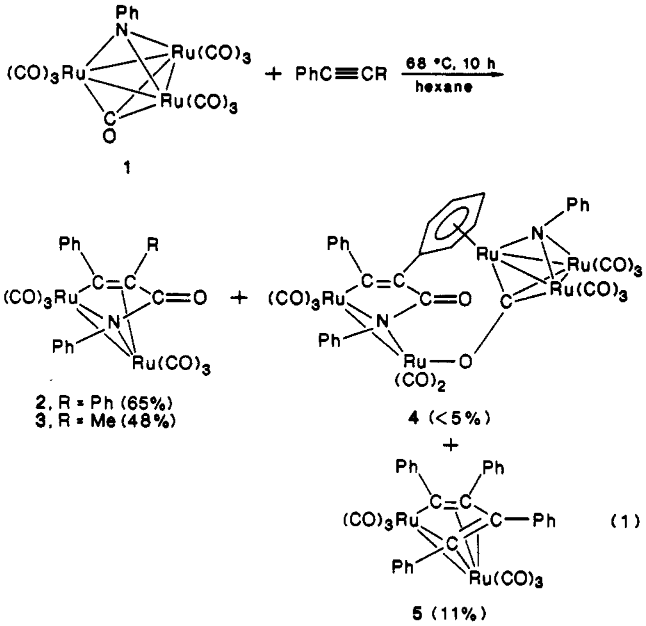
Summary: The μ_3-nitrene cluster 1 reacts with PhC≡CPh to give the binuclear metallapyrrolidone complex 2 formed by combination of the alkyne with CO and the nitrene ligand. This species further reacts with PhC≡CPh and CO to form pentaphenylpyridone and 1,3,4-triphenylmaleimide, respectively. Low-yield products accompanying the synthesis of 2 are the metallacyclopentadiene complex 5 and the unusual Ru_5 cluster 4. The structures of 2 and 4 have been crystallographically established.

The chemistry of low-valent metal carbene complexes has been extensively investigated and many such compounds have found impressive synthetic utility.[1] In contrast, the chemistry of nitrene ligands bound to low-valent metals remains relatively unexplored,[2] even though such ligands have been invoked as intermediates in several catalytic reactions.[3] In our efforts to develop the chemistry of μ_3-nitrene ligands in metal clusters, we previously demonstrated the coupling of nitrenes with carbene and acyl ligands to give imidates,[4] carbamates,[5] and benzanilide.[5] Herein we report the first examples of coupling of μ_3-nitrenes with alkynes and CO to give binuclear metallapyrrolidone complexes from which pyridones and imides subsequently derive.

The metallapyrrolidone complex 2[6] forms in good yield when the μ_3-nitrene cluster 1[7] is heated in the presence of PhC≡CPh (eq 1). Complex 2 has been crystallographically characterized (Figure 1).[8] The Ru atoms of 2 are



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(1) (a) Brown, F. J. *Prog. Inorg. Chem.* 1980, *27*, 1. (b) Casey, C. P. *React. Intermed.* 1985, *3*, 109. (c) Kreissl, F. R.; Doetz, K. H.; Weiss, K. In *Transition Metal Carbene Complexes*; Verlag Chemie Weinheim, 1983. (d) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*, University Science Books: Mill Valley, CA, 1980; pp 91-103.

(2) For reviews, see: (a) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* 1980, *31*, 123-175. (b) Cenini, S.; La Monica, G. *Inorg. Chim. Acta* 1976, *18*, 279.

(3) (a) Cenini, S.; Pizzotti, M.; Crotti, C.; Porta, F.; Monica, G. L. *J. Chem. Soc., Chem. Commun.* 1984, 1286. (b) Alper, H.; Hashem, K. E. *J. Am. Chem. Soc.* 1981, *103*, 6515. (c) L'eplattenier, F.; Matthys, P.; Calderazzo, F. *Inorg. Chem.* 1970, *9*, 342. (d) Andrew, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* 1979, *101*, 7225. (e) Dawoodi, Z.; Mays, M. J.; Henrick, K. *J. Chem. Soc., Dalton Trans.* 1984, 433. (f) Bhaduri, S.; Gopalkrishnan, K. S.; Clegg, W.; James, P. G.; Sheldrick, G. M.; Stalke, D. *J. Chem. Soc., Dalton Trans.* 1984, 1765. (g) Bernhardt, W.; Schnering, V. C.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* 1986, *25*, 279.

(4) Williams, G. D.; Geoffroy, G. L.; Whittle, R. R.; Rheingold, A. L. *J. Am. Chem. Soc.* 1985, *107*, 729.

(5) Williams, G. D.; Geoffroy, G. L.; Rheingold, A. L., to be submitted for publication.

(6) 2: IR (hexane) ν_{CO} 2091 (m), 2066 (vs), 2020 (vs), 2002 (s), 1717 (m) cm^{-1}; m/z (EI) 669; ^1H NMR (CD_2Cl_2) δ 7.26 (br, Ph). Anal. Calcd: C, 56.04; H, 2.74. Found: C, 55.89; H, 2.70.

(7) (a) Bhaduri, S.; Gopalkrishnan, K. S.; Sheldrick, G. M.; Clegg, W.; Stalke, D. *J. Chem. Soc., Dalton Trans.* 1983, 2339. (b) For an improved preparation from $Ru_3(CO)_{12}$ and PhNO see: Smieja, J. A.; Gladfelter, W. L. *Inorg. Chem.* 1986, *25*, 2667.

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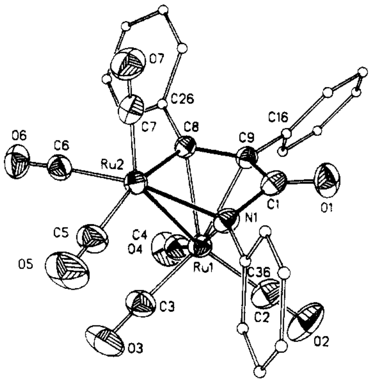
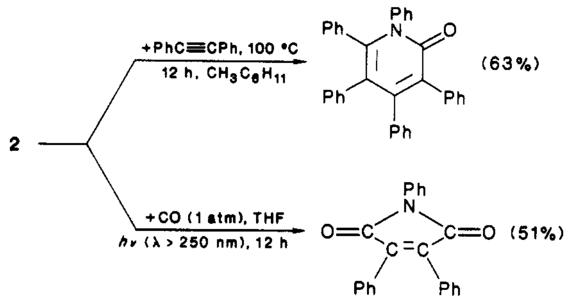


Figure 1. Molecular structure and labeling scheme for **2** (40% thermal ellipsoids). Bond distances (Å) and bond angles (deg): Ru(1)–Ru(2), 2.677 (1); Ru(1)–N(1), 2.164 (3); Ru(2)–N(1), 2.136 (3); Ru(1)–C(8), 2.299 (3); Ru(1)–C(9), 2.296 (3); Ru(2)–C(8), 2.073 (3); N(1)–C(1), 1.437 (5); C(1)–C(9), 1.494 (5); C(9)–C(8), 1.425 (5); C(1)···Ru(1), 2.598 (3); Ru(1)–N(1)–Ru(2), 77.0 (1); Ru(2)–N(1)–C(1), 90.0 (2); N(1)–C(1)–C(9), 106.3 (3); C(1)–C(9)–C(8), 114.7 (3); C(9)–C(8)–Ru(2), 116.3 (2); N(1)–C(1)–O(1), 125.0 (3)°; C(9)–C(1)–O(1), 128.3 (4).

joined by a single Ru-Ru bond (2.6767 (5) Å) and are bridged by the μ-PhC=C(Ph)C(O)NPh ligand which derives from combination of the nitrene ligand with CO and the added alkyne. This ligand is similar to that found in the two recently reported compounds $Cp_2Rh_2(\mu\text{-}CF_3{=}C(CF_3)C(O)NPh)$ (**6**)[9] and $Fe_2(CO)_6\{\mu\text{-}EtOC{=}C(Me)C(O)N(N{=}CPh_2)\}$,[10] and the structural parameters for the bridging ligands in the three compounds are similar. Interestingly, compound **6** was prepared by the reaction of an alkyne complex with a source of phenylnitrene (PhN_3, PhNCO) whereas **2** derives from addition of alkyne to a preformed nitrene cluster, formally the reverse order of reagent addition. Although the mechanism of formation of **2** is unknown, the coupling of the μ_3-NPh ligand with CO has so far been found to occur only in the presence of alkyne. The sole reaction observed when **1** was heated in the presence of CO alone was disproportionation to $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$[7] and $Ru_3(CO)_{12}$.[11] Reaction of **1** with MeC≡CPh proceeds in a regiospecific manner, generating only **3**[12] with the phenyl substituent on the carbon adjacent to Ru (eq 1).

A low yield product of reaction 1 is the unusual pentaruthenium complex **4**.[13] The molecular structure of this species (Figure 2)[14] shows it to result from combination of **1** with **2**, and indeed this direct reaction in cyclohexane (81 °C, 20 h) gave **4** in 49% yield. In forming **4**, a phenyl substituent of the μ-PhC=C(Ph)C(O)NPh ligand of **2** has replaced three CO's on a single Ru atom of **1** and is coordinated in an η^6 fashion. In turn, one of the Ru atoms of **2** has lost a CO, and the μ_3-carbonyl ligand of **1** is bound in an isocarbonyl fashion to this Ru. This portion of the structure is similar to that observed in such compounds as $Cp_2M(OCCo_3(CO)_9)_2$ (M = Zr, Hf)[15] in which the μ_3-carbonyl oxygen is attached to an oxophilic early transition metal. To our knowledge **4** is the first example of such a linkage in a compound containing only late transition metals. The Ru(4)–O(13) distance of 2.23 (1) Å is only slightly longer than typical Ru–O single bond distances of 2.1 Å (e.g., $(Ru\text{-}O)_{av}$ = 2.15 Å in $Ru_4(CO)_{10}(C{=}CH\text{-}t\text{-}Pr)(OH)(PPh_2)$[16a]; 2.12 Å in $[(\eta^6\text{-}C_6H_6)Ru(OH)](SO_4)_2\cdot 12H_2O$[16b]). Also formed in reaction 1 is the known[17] metallacyclopentadiene complex **5**, which presumably results from combination of PhC≡CPh with $Ru(CO)_x$ fragments liberated in the **1** → **2** conversion.

Scheme I



Complex **2** is an interesting precursor to the organics pentaphenylpyridone[18] and 1,3,4-triphenylmaleimide[19] formed by the reactions with excess alkyne and CO (Scheme I). The latter reaction proceeds efficiently only upon photolysis; unreacted **2** is recovered in ~90% yield from the thermal reaction with CO (1200 psi, 120 °C, 48 h). Both of these transformations have precedent in the conversion of a mononuclear nickelapyrrolidone complex into these products[20] and in the use of Co and Ni complexes to catalyze the formation of pyridones from alkynes and isocyanates.[21] The reactions of Scheme I are the first

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[8] Crystal data: monoclinic, $P2_1/c$, $a = 21.492$ (5) Å, $b = 7.840$ (1) Å, $c = 15.819$ (4) Å, $\beta = 100.6$ (2)°, $V = 2619.4$ (9) Å^3, $Z = 4$, D(calcd) = 1.692 g cm^{-3}; yellow crystal, 0.26 × 0.31 × 0.32 mm; 6042 reflections collected and absorption corrected (T_{max}/T_{min} = 0.436/0.393); μ = 17.4 cm^{-1} (Mo Kα); 4° ≤ 2θ ≤ 53°; 5416 unique reflections R(int) = 1.67%, and 4417 ($F_o \geq 3\sigma(F_o)$) used in the solution (direct methods) and refinement. For 299 parameters (all non-H atoms anisotropic, phenyl rings rigid, planar hexagons, and H atoms calculated), R_F = 2.99%, R_{wF} = 3.53%, GOF = 1.098, Δ/σ = 0.09, and highest peak, final difference map = 0.46 e/Å^3. All programs SHELXTL (5.1), Nicolet Corp., Madison, WI.

[9] Dickson, R. S.; Nesbit, R. J.; Pateras, H.; Baimbridge, W. *Organometallics* **1985**, *4*, 2128.

[10] Null, D.; Dahan, F.; Mathieu, R. *Organometallics* **1986**, *5*, 1278.

[11] Han, S. H.; Williams, G. D., unpublished observation.

[12] **3**: IR (CH_2Cl_2) ν_{CO} 2093 (m), 2066 (vs), 2020 (vs), 2002 (m, sh), 1686 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 7.31 (br, Ph), 2.27 (s, CH_3); m/z (EI) 607. Anal. Calcd: C, 43.49; H, 2.14. Found: C, 43.59; H, 2.27. This complex has been crystallographically characterized; details will be published in the full paper.

[13] **4**: IR (hexane) ν_{CO} 2085 (s), 2079 (s), 2067 (s), 2060 (s), 2047 (s), 2039 (s), 2026 (vs), 2008 (s), 2002 (m), 1991 (s), 1958 (m), 1850 (w, br), 1736 (w, br), 1692 (w) cm^{-1}; m/z (EI) 1179 (M – 2CO).

[14] Crystal data: monoclinic, $P2_1/c$, $a = 15.313$ (5) Å, $b = 27.319$ (10) Å, $c = 20.593$ (7) Å, $\beta = 102.46$ (3)°, $V = 8412$ (7) Å^3, $Z = 8$, D(calcd) = 1.942 g cm^{-3}; deep red crystal, 0.31 × 0.32 × 0.34 mm, 10590 reflections collected and absorption corrected (T_{max}/T_{min} = 0.722/0.640), μ = 17.9 cm^{-1} (Mo Kα), 4° ≤ 2θ ≤ 42° (limited by weakness of diffraction intensity), 9025 unique reflections, R(int) = 1.08%, and 5783 ($F_o \geq 3\sigma(F_o)$) used in the solution (direct methods) and refinement. The asymmetric unit consists of two crystallographically independent but chemically identical molecules. For 986 parameters (all non-H atoms anisotropic, phenyl rings rigid, planar hexagons except for the η^6-ring), and H atoms calculated, R_F = 5.92%, R_{wF} = 5.78%, GOF = 1.278, Δ/σ = 0.10, highest peak, and final difference map = 0.96 e/Å^3. Programs as used in ref 8.

[15] Stutte, B.; Baetzel, V.; Boese, R.; Schmid, G. *Chem. Ber.* **1978**, *111*, 1603.

[16] (a) Carty, A. J.; MacLaughlin, S. A.; Tayler, N. J. *J. Chem. Soc., Chem. Commun.* **1981**, 476. (b) Gould, R. O.; Jones, C. L.; Robertson, D. R.; Stephenson, T. A. *J. Chem. Soc., Chem. Commun.* **1977**, 222.

[17] Sears, C. T., Jr.; Stone, F. G. A. *J. Organomet. Chem.* **1968**, *11*, 644.

[18] Spectral data: IR (KBr) ν_{CO} 1640 cm^{-1}; m/z (EI), calcd for $C_{35}H_{25}NO$ 475.1936, found 475.1919 (M$^+$).

[19] Spectral data: IR (CH_2Cl_2) ν_{CO} 1725 cm^{-1}; m/z (EI) 325 (M$^+$).

[20] Hoberg, H.; Oster, B. W. *Synthesis* **1982**, 324; *J. Organomet. Chem.* **1982**, *234*, C35; **1983**, *252*, 359.

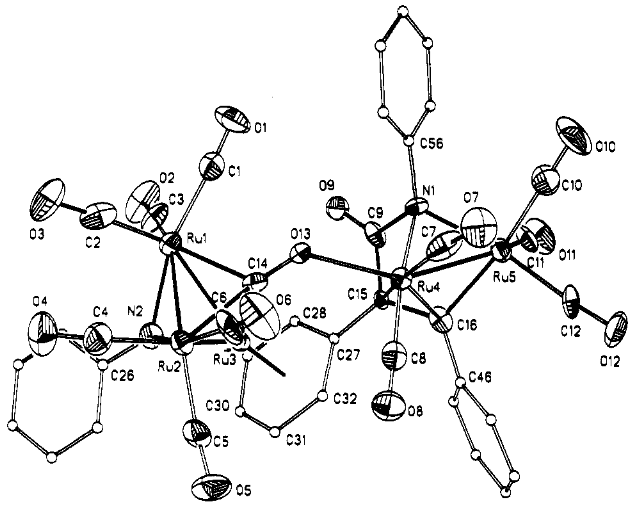

Figure 2. Molecular structure and labeling scheme for 4 (40% thermal ellipsoids). Only one of the chemically indistinguishable but independent molecules in the asymmetric unit is shown. Bond distances (Å) bond angles (deg): Ru(1)–C(14), 2.18 (1); Ru(2)–C(14), 2.21 (1); Ru(3)–C(14), 1.98 (1); ⟨av⟩ Ru(3)–C(η^6-C_6H_5), 2.27 (2); C(14)–O(13), 1.27 (2); O(13)–Ru(4); 2.23 (1); ⟨av⟩ Ru–C(14)–Ru, 79.7 (6); Ru(4)–O(13)–C(14), 128 (1).

demonstration of such chemistry from a binuclear metallapyrrolidone complex.

It is interesting to compare the chemistry described herein to the recently reported reactions of alkynes with the μ_3-phosphinidene iron analogue of 1, $Fe_3(\mu_3\text{-}PC_6H_4OCH_3)(CO)_{10}$.[22] These reactions gave trinuclear products from either substitution of alkyne for a cluster CO (photolysis) or insertion of the alkyne into an Fe–P bond (thermolysis). In contrast to the results reported herein, no coupling of the phosphinidene ligand with CO was observed, further illustrating the significant reactivity differences between isoelectronic μ_3-nitrene and μ_3-phosphinidene ligands.[4]

It is clear from this and related studies that μ_3-nitrene ligands in metal clusters can combine with a variety of other ligands including hydrides,[3f,g] carbenes,[4] acyls,[5] methoxycarbonyls,[5] and now alkynes. The further reactivity of this ligand is under exploration in our laboratory, with current efforts directed toward its reactions with olefins and other unsaturated organic substrates.

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Registry No. 1, 51185-99-0; 2, 105121-10-6; 3, 105102-79-2; 4, 105121-11-7; 5, 33310-08-6; PhC≡CMe, 673-32-5; PhC≡CPh, 501-65-5; $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$, 51233-18-2; $Ru_3(CO)_{12}$, 15243-33-1; Ru, 7440-18-8.

Supplementary Material Available: Tables of atomic positional parameters, anisotropic thermal parameters, bond lengths and angles, and calculated hydrogen atom positions for 2 and 4 (15 pages); listings of structure factors for 2 and 4 (61 pages). Ordering information is given on any current masthead page.

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[21] Hong, P.; Yamazaki, H. *Tetrahedron Lett.* 1977, *15*, 1333; *Synthesis* 1977, 50.

[22] Knoll, K.; Orama, O.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 976.

Chemistry of the Organochromium(I) Radical $CpCr(CO)_3\cdot$. X-ray Structure of a Stable Derivative, $CpCr(CO)_2(PPh_3)\cdot$

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Summary: The metal-metal-bonded dimer $[CpCr(CO)_3]_2$ (II) reacts (a) with Bu_3SnH to give $CpCr(CO)_3H$ and $CpCr(CO)_3SnBu_3$ and (b) with methyl iodide to give $CpCr(CO)_3I$ and $CpCr(CO)_3Me$. Both reactions appear to involve the chromium-centered radical $CpCr(CO)_3\cdot$, formed spontaneously via dissociation of II. The X-ray crystal structure of the chromium-centered radical $CpCr(CO)_2(PPh_3)\cdot$ has been determined; the compound is isostructural with the 18-electron species $CpMn(CO)_2(PPh_3)$ but exhibits a deformation which may be attributed to the electron "hole".

We have recently reported a mechanistic investigation, involving CIDNP studies, of the hydrometalation ("insertion") and hydrogen-transfer reactions of $HMn(CO)_5$ and $CpFe(CO)_2H$ with conjugated dienes.[1] In an attempt to extend this work to similar reactions of the hydride $CpCr(CO)_3H$[2] (I), we have observed no CIDNP polarizations but did to our surprise observe coalescence of the cyclopentadienyl ^1H NMR resonance of I with that of the reaction byproduct $[CpCr(CO)_3]_2$ (II). Although we can offer for this behavior no obvious rationalization involving direct exchange between I and II, the chromium–chromium bond of the latter is sufficiently weak[3] that II dissociates slightly in solution to form the paramagnetic monomer $CpCr(CO)_3\cdot$ (III).[4] Thus one may postulate direct hydrogen atom exchange between I and III, i.e.

$$[Cr]H + [Cr] \rightarrow [Cr]\cdots H\cdots[Cr] \rightarrow [Cr] + H[Cr] \quad (1)$$

$$[Cr] = CpCr(CO)_3$$

Precedent for this reaction is found in the facile transfer of hydrogen from $CpMo(CO)_3H$ to photogenerated $CpW(CO)_3\cdot$,[5] and indeed, atom abstraction reactions are a characteristic process of transition-metal-centered radicals such as III.[6] In the system under consideration here,

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[1] (a) Thomas, M. J.; Shackleton, T. A.; Wright, S. C.; Gillis, D. J.; Colpa, J. P.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* 1986, 312. (b) Wassink, B.; Thomas, M. J.; Wright, S. C.; Gillis, D. J.; Baird, M. C., submitted for publication.

[2] Miyake, A.; Kondo, H. *Angew. Chem., Int. Ed. Engl.* 1968, *7*, 631.

[3] Adams, R. D.; Collins, D. E.; Cotton, F. A. *J. Am. Chem. Soc.* 1974, *96*, 749.

[4] (a) Madach, T.; Vahrenkamp, H. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* 1978, *33B*, 1301. (b) Madach, T.; Vahrenkamp, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1979, *348*, 573. (c) Goh, L.-Y.; D'aniello, M. J.; Slater, S.; Muetterties, E. L.; Tavanaiepour, I.; Chang, M. I.; Fredrich, M. F.; Day, V. W. *Inorg. Chem.* 1979, *18*, 192.

[5] Hoffman, N. W.; Brown, T. L. *Inorg. Chem.* 1978, *17*, 613.

[6] (a) Brown, T. L. *Ann. N. Y. Acad. Sci.* 1980, *33*, 80. (b) Wrighton, M. S.; Graff, J. L.; Luong, J. C.; Reichel, C. L.; Robbins, J. L. In *Reactivity of Metal-Metal Bonds*; Chisholm, M. H., ed.; *ACS Symposium Series* 155; American Chemical Society: Washington, DC, 1981; p 85. (c) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* 1975, *97*, 2065. (d) Abrahamson, H. B.; Wrighton, M. S. *Inorg. Chem.* 1978, *17*, 1003. (e) Kidd, D. R.; Cheng, C. P.; Brown, T. L. *J. Am. Chem. Soc.* 1978, *100*, 4103. (f) Wegman, R. W.; Brown, T. L. *Organometallics* 1982, *1*, 47. (g) McCullen, S. B.; Brown, T. L. *J. Am. Chem. Soc.* 1982, *104*, 7496. (h) Herrick, R. S.; Herrinton, T. R.; Walker, H. W.; Brown, T. L. *Organometallics* 1985, *4*, 42. Hankel, J. M.; Lee, K.-W.; Rushman, P.; Brown, T. L. *Inorg. Chem.* 1986, *25*, 1852.

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